SEMIEMPERICAL ONE CENTRE AND TWO CENTRE ELECTRON REPULSION INTEGRALS

S. PAHARI AND A. K. KAR

DEHARTMENT OF APPLIED CHEMISTRY, INDIAN INSTITUTE OF TECHNOLOGY, KHARAGPUR

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ABSTRACT. One centre and Two centre electron repulsion integrals were calculated for the π-electrons in C-C, O-O C-O, N-N, C-N, N-O, C-Cl, Cl-Cl etc with the help of several equations and the corresponding integrals for ethylene, benzene and formaldehyde were reported. Fisher-Hjalmar's equation (1964) for two centre and the equation (0.86E/R+7.86) e.v, where E is the electronegativity of the atom in electron volt in Pauling's scale and R is the Slater's atomic radius, for one centre electron repulsion integral seems to be the best choice.

In the last few years semiemperical M.O. theory has achieved considerable success, particularly the method of Pariser and Parr (1953) for the calculation of electronic spectre of conjugated systems and that of Pople (1953) for the calculation of ionization potential and bond distance etc., of the same type of molecules. Several simple modifications of the methods were proposed later with a view to better correlating the data.

Any such method require the evaluation of a number of electrons repulsion integrals e.g.,

$$\int\int x_p^*(1)\, x_q^*(1)\, \frac{e^2}{r_{12}}\, x_R(2) x_S(2)\, \delta T_1\, \delta T_2 = (p\,|\,qrs) \qquad (1)$$

where x_n etc. are atomic orbitals.

Extract evaluation using Slaters, a, σ's were carried out (Parr *et. al*, 1950), but the results in predicting molecular parameters were not encouraging, leaving apart the tedious calculations. That is the reason of use semi-empierical parameters and introducing the idea of zero differential overlap, the required integrals are reduced to the evaluation of $(pp\,|\,pp)$ [2 electron 1 centre] and $(pp\,|\,qq)$ [2 electron 2 centre] only.

Here we have defined as usual :

$$(pp\,|\,pp) = I_p - E_p \qquad \ldots\ (2)$$

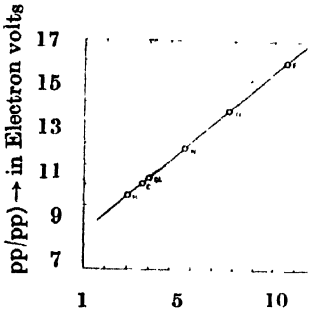
where I_p and E_p are valence state ionization potential and electron affinity of an atom respectively. The data of Pritchard and Skinner (1954-55) and L. Oleari

et al (1966) are used. For many atoms I_p and E_p data are not available, so from a plot of (fig. 1), $|(pp\ pp)$ vs E/r a linear relation is obtained (where E is the electronegativity in Paulings scale and r is the Slaters atomic radius (Slater 1953) :

$$(pp\,|\,pp) = 0{\cdot}8642\ E/r + 7{\cdot}86 \qquad \ldots\ (3)$$

which can be used to calculate $(pp\,|\,pp)$ of any atom.

$(pp\,|\,qq)$ is calculated in one set for $r \geqslant 2{\cdot}80\ a^\circ$ (hard sphere model of Parr, 1952) by :



E/T → Electronegativity Slater's Radius.

Fig. 1.

$$(pp\,|\,qq) = \frac{7{\cdot}1975}{r}\left\{\left[1+\left(\frac{R_p+R_q}{2r}\right)^2\right]^{\frac{1}{2}}+\left[1+\left(\frac{R_p-R_q}{2r}\right)^2\right]^{\cdot}\right\} \qquad \ldots\ (4)$$

where $R_p = \dfrac{4.597}{Z_p} \times 10^{-8}$ cm and Z_p = Slater's effective nuclear charge ... (5)

For the distances less than $2{\cdot}80a^\circ$ $(pp\,|\,qq)$ is expressed as

$$ar + br^2 = \tfrac{1}{2}\,[(pp\,|\,pp)+(qq\,|\,qq)] - (pp\,|\,qq) \qquad \ldots\ (6)$$

a and b are evaluated for a set by solving equation (6) for $r = 2{\cdot}80\ a^\circ$ and $3{\cdot}70\ a^\circ$. In this way $(pp\,|\,qq)$ intergrals are evaluated for C-C, C-O, O-O, N-N, C-N, N-O etc. and are expressed as a function of r (table 1).

$(pp\,|\,qq)$ are also evaluated in another set by using an equation almost like Fisher-Hjalmars (1965) where $(pp\,|\,qq)$ is defined by equation (4) for $r \geqslant 2{\cdot}794\ a^\circ$ and for $r \leqslant 2{\cdot}794\ a^\circ$.

$$(pp\,|\,qq) = \tfrac{1}{2}\,[(pp\,|\,pp)+(qq\,|\,qq)] + ar^2 + br^3 + cr^4 \qquad \ldots\ (7)$$

a, b, and c are evaluated for C-C, C-O, C-N, C-Cl etc. from equation (4) for $r = 2{\cdot}794$, $3{\cdot}7$ and $3{\cdot}4\ a^\circ$. The results are listed in table 1.

The corresponding values by the two methods are calculated for ethylene, for-maldehyde, benzene and are shown in table II.

Fisher-Hjalmars equation (1964) for $(pp\,|\,qq)$:

$$(pp\,|\,qq) = \tfrac{1}{2}(\mu_p+\mu_q)[8{\cdot}7542-1{\cdot}4005\rho+0{\cdot}16724\rho^2-0{\cdot}00961\rho^3] \qquad (8)$$

where $$\rho = \frac{\mu_p+\mu_q}{2} R$$

is a very general one and integrals for the distances in benzene, ethylene and formaldehyde are also calculated with the help of this equation and are listed for comparison.

TABLE I

$(pp\,|\,qq)$ for $r \leqslant 2{\cdot}80$ and $2{\cdot}794$ a°

Column A represents a and b of eqn. (6) for $r \leqslant 2{\cdot}80$ a° and column B represents a, b and c of eqn. (7) (modified Fisher-Hjalmar's eqn.) for $r \leqslant 2{\cdot}794$ a°. For r grater than these distances $(pp\,|\,qq)$ is given by eqn. (4).

$pp\,\|\,qq$ for bond	$-[(pp\,\|\,qq)+(pp\,\|\,qq)]_{e.v.}$	Column A		Column B		
		a	b	a	b	c
C — C	11.08[1]	0.1167	−2.337	−1.734	0.4669	−0.03716
O — O	14.52[1]	0.486	−4.63	−3.8249	1.3221	−0.1343
C — O	12.80[1]	0.2982	−3.486	−2.047	+0.4358	−0.01529
N — N	12.98[1]	+0.3203	−3.6142	−2.8617	0.9225	−0.08825
	12.74[2]	0.2972	−3.464	—	—	—
C — N	12.02[1]	0.2172	−2.9687	−2.2929	0.6926	−0.06257
	11.91[2]	0.2065	−2.8991	—	—	—
N — O	13.75[1]	0.4041	−4.1363	−3.3424	1.1218	−0.1112
	13.58[2]	0.3876	−4.0294	—	—	—
Cl — Cl	11.30[1]	0.1998	−2.7264	—	—	—
	11.27[2]	0.1919	−2.7076	—	—	—
C — Cl	11.19[1]	0.1399	−2.4666	−1.8512	0.5097	−0.041005
	11.75[2]	0.1384	−2.4561	—	—	—
F — F	16.70[1]	0.7037	−6.0474	—	—	—
	17.33[2]	0.7653	−6.4473	—	—	—
C — F	13.89[1]	0.4102	−4.1941	−1.7279	0.8243	−0.1134
	14.205[2]	0.4406	−4.3917	—	—	—
S — S	10.81[1]	0.1408	−2.377	—	—	—
C — S	10.945[1]	0.1291	−2.355	−1.7230	0.4618	−0.036
S — O	12.665[1]	0.3145	−3.519	—	—	—

[1] Data of L. Oleari *et al.*, (1966).
[2] Data of Pritchard and Skinner (1953).

TABLE II

Subs.	Integrals		Distance in a°	Using eqn. 6	Using eqn. 7	Using eqn. 8+
C_2H_4	(11/11)	ev	0	11.08	11.08	11.08
	(11/22)	ev	1.337	8.1636	8.9775	7.1926
CH_2O	(11/11)C	ev	0	11.08	11.08	11.08
	(11/11)O	ev	0	14.52	14.52	14.52
	(11/22)C=O	ev	1.210	8.1452	9.6823	9.7149
Benzene	(11/11)	ev	0	11.08	11.08	11.08
	(11/22)	ev	1.397	8.043	8.8273	7.9377
	(11/33)	ev	2.42	6.088	6.26078	5.61760
	(11/44)	ev	2.794	5.462	5.4236	4.5152

+ μ Values are taken from Mulliken, *et al.*, (1949).

As it is evident from Table-II, the values for (pp/qq) obtained by equation (7) are comparatively higher, while those obtained by the use of equation (8) are comparatively lower for hydrocarbons. However, the reverse is the case for heteromolecules with equation (8) in comparison to those of equation (6) or equation (7). Thus although the results obtained by equation (8) are not exactly identical, but are in the expected order as seen from Parriser and Parr (Loc.cit).

Therefore, apparently equation (3) for (pp/qq) and equation (8) for (pp/qq) seems to be the simplest and the best choice.

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REFERENCES

Inga Fisher-Hjalmars, 1964, *Moleculars Orbitals in Chemistry, Physics and Biology, A tribute to R. S. Mulliken*, edited by P. O. Lowden and B. Pullman, Academic Press, pp. 361.

———, 1965, *Tetrahendron*, **19**, 1805.

Mulliken, R. S., Rieke, C. M., Orloff, O., and Orloff, H., 1949, *J. Chem. Phys.*, **17**, 1248.

Oleari, L., Sipio, L. D. and Michelis, G. P., 1966, *Molecular Physics.*, **10**, 97,

Pariser, R. and Parr, T. G., 1953, *J. Chem. Phys.*, **21**, 466, 767.

Parr, R. G., Craig, D. P. and Ross, I. G., 1950, *J. Chem. Phys.*, **18**, 1561,

Pople, J. A., 1953, *Trans. Faraday. Soc.*, **49**, 1375.

Pritchard, H. O. and Skinner, H. A., 1953, *Trans. Faraday. Soc.*, **49**, 1254.

———, 1955, *Chem. Rev.*, **55**, 748.

Slater, J. G., 1953, *Quantum Theory of Matter*, McGraw Hill, Table 6·42, p. 146.